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Comparison of cation-ordered $P2_1/c$ leucite structures with stoichiometry $K_2X^{2+}Si_5O_{12}$ ($X = Mg, Fe, Co, Zn$)

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Introduction

Synthetic anhydrous analogues of the silicate framework minerals **leucite** ($KAlSi_3O_8$) and **pollucite** ($CsAlSi_3O_8$) can be prepared with the general formulae $A_2BSi_5O_{12}$ and $ACSi_2O_6$, where A is a monovalent alkali metal cation, B is a divalent cation and C is a trivalent cation. These structures all have the same topology with B and C cations partially substituting onto tetrahedrally coordinated sites (T-sites) in the silicate framework and charge balancing A cations sitting in extra-framework channels. The A cations can be replaced by ion exchange and these materials are of potential technological interest as storage media for radioactive Cs from nuclear waste [1].

We have used X-ray and neutron powder diffraction to determine and Rietveld [2] refine the crystal structures of many different leucite analogues [3-11], one of these was for $K_2MgSi_5O_{12}$ [5], this was the first known leucite structure with ordered T-site cations and was determined from synchrotron X-ray powder diffraction data on the old Daresbury SRS [12, 13]. In this poster we report the Rietveld refinements of the crystal structures of three more cation ordered leucite analogues, $K_2X^{2+}Si_5O_{12}$ where $X = Fe, Co$ or Zn .

Synthesis

The samples were made from appropriate stoichiometric mixtures of K_2CO_3 , SiO_2 , Fe_2O_3 ($X = Fe$), CoO ($X = Co$) and ZnO ($X = Zn$). For $X = Fe$ the sample was reduced from Fe^{3+} to Fe^{2+} [14].

Data collection and analysis

All samples were mounted on low-background silicon wafers prior to ambient temperature X-ray powder diffraction data. Data were collected for the $X = Fe$ sample on a PANalytical X'Pert Pro MPD using $Cu K\alpha$ X-rays and an X'Celerator area detector. For the other two samples data were collected on a PANalytical Empyrean diffractometer with a PIXCEL-3D area detector. For $X = Zn$, $Cu K\alpha$ X-rays were used and for $X = Co$, $Co K\alpha$ X-rays were used. Analyses of the powder diffraction data showed that in all samples the major phase was isostructural with the $P2_1/c$ structure of $K_2MgSi_5O_{12}$ [5]. Rietveld refinements were done using FULLPROF [15], using the structure of $K_2MgSi_5O_{12}$ as a starting model with X cations replacing Mg. However, for $X = Co$ a second mica phase with the stoichiometry $KCo_3(CoSi_3O_{10})OH_2$ (based on $KCo_3(AlSi_3O_{10})OH_2$ [16]) was included in the refinement as a 4.7(1) wt.% minor phase. For $X = Fe$ and Zn single-phase refinements were done.

Figures 1, 2 and 3 show the Rietveld difference plots for these structures. Table 1 shows the comparison of some refined structural parameters for $K_2MgSi_5O_{12}$ and $X = Fe, Zn$ and Co . Ionic and crystal radii are from Shannon [17]. The tetrahedral angle variance [18] shows the distortion of tetrahedral units in the silicate framework. Figure 4 shows a VESTA structure [19] plot for $K_2FeSi_5O_{12}$, this shows how the Si and Fe framework cations are ordered onto separate T-sites.

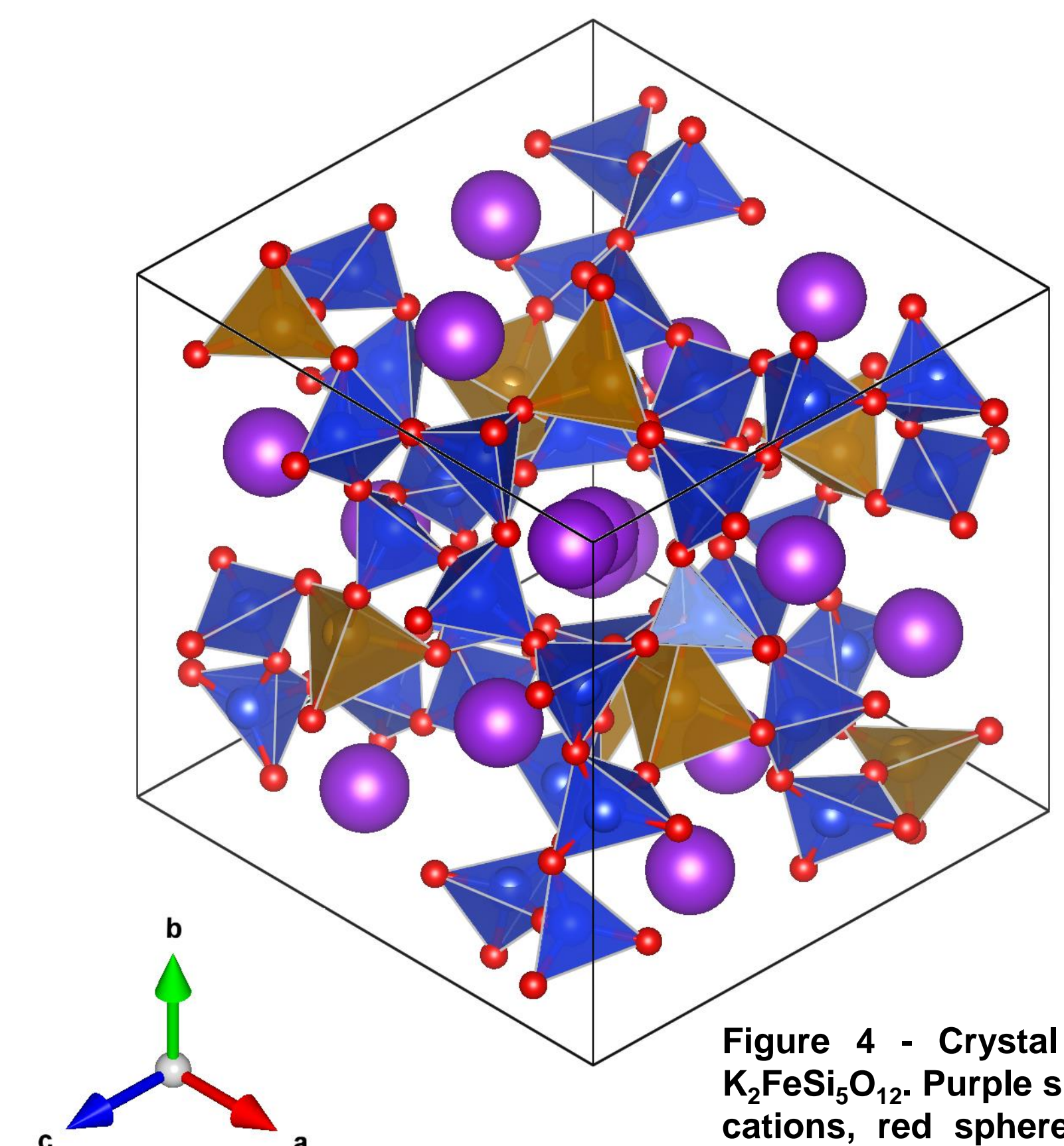
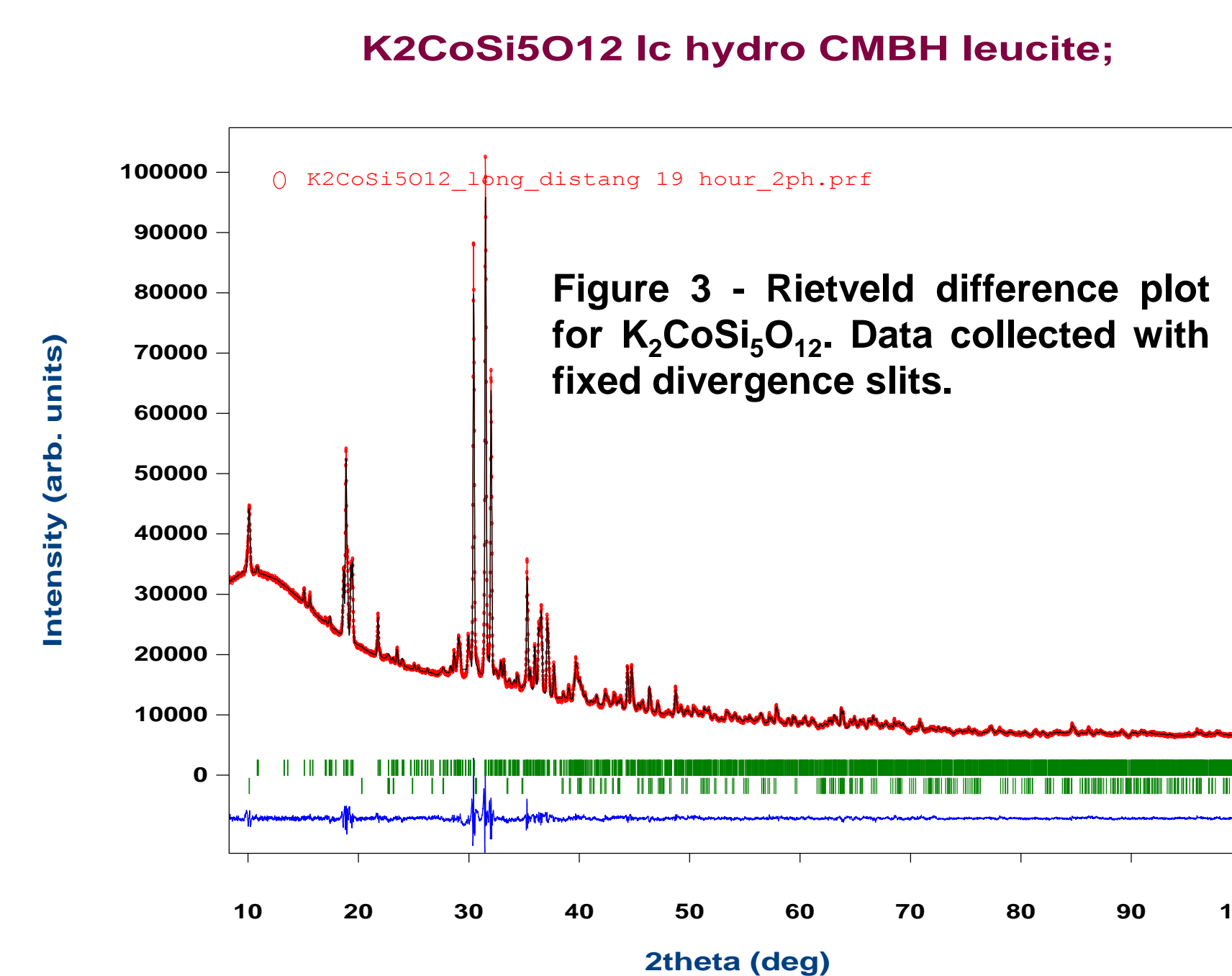
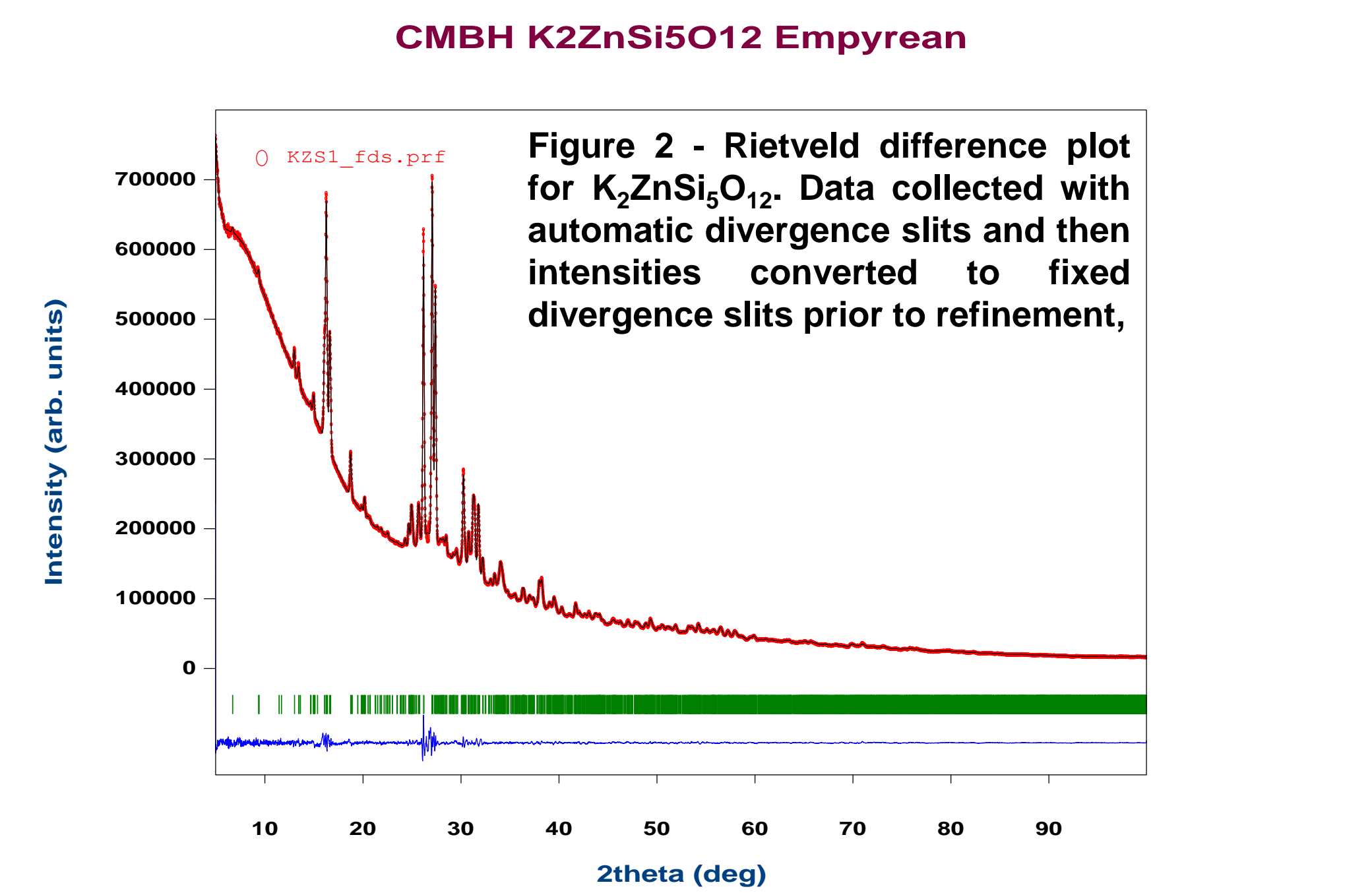
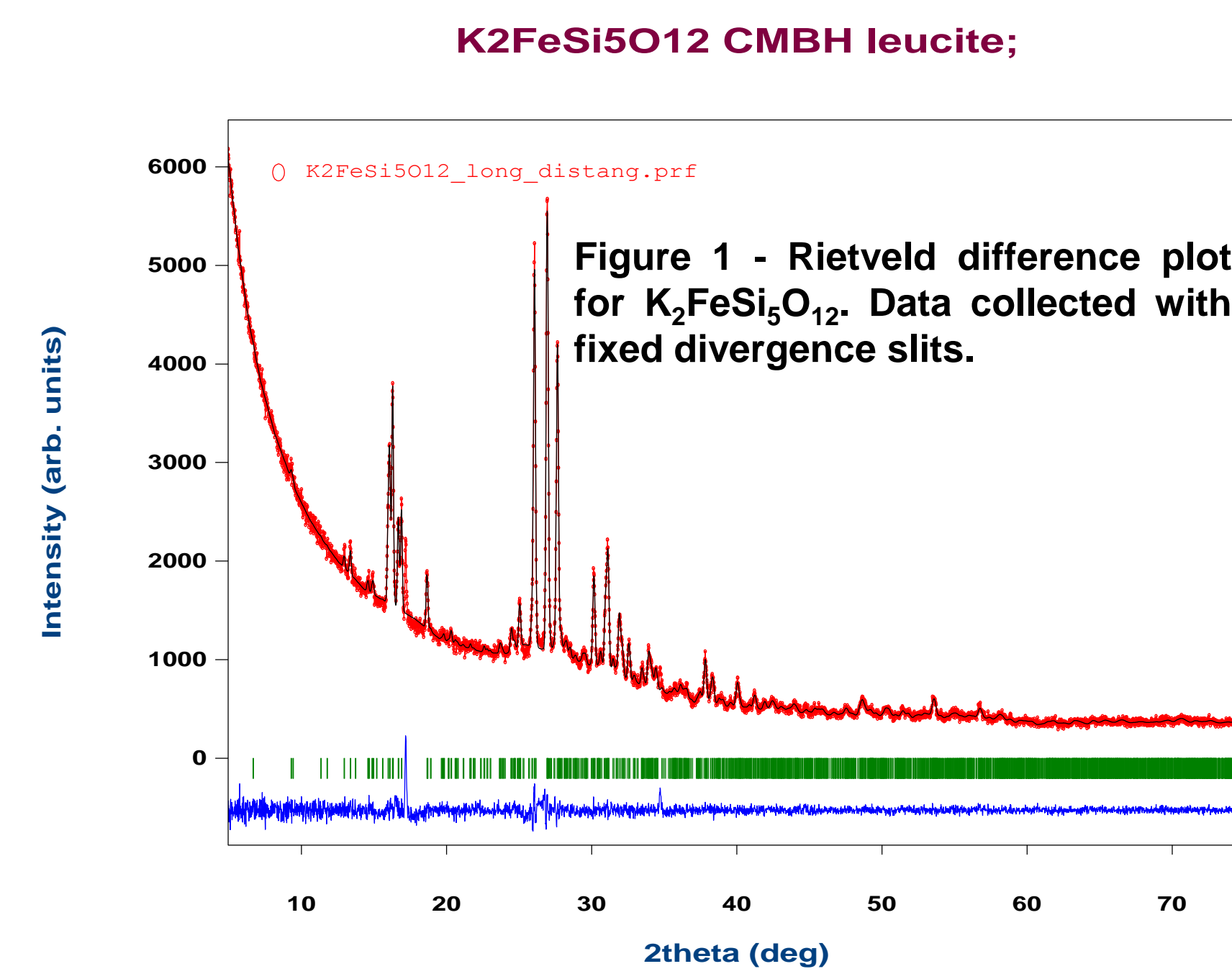


Figure 4 - Crystal structure plot for $K_2FeSi_5O_{12}$. Purple spheres represent K^+ cations, red spheres O^{2-} anions, blue tetrahedra represent SiO_4 units and light brown tetrahedra represent FeO_4 units.

Table 1 - comparison of refined structural parameters

X	Mg	Fe	Zn	Co
a (Å)	13.168(5)	13.2574(5)	13.1773(2)	13.1878(1)
b (Å)	13.652(1)	13.6739(6)	13.6106(2)	13.6350(2)
c (Å)	13.072(5)	12.9240(5)	13.0248(2)	12.9876(1)
β (°)	91.69(5)	93.048(3)	91.70(6)	91.999(8)
V (Å ³)	2348(2)	2339.6(2)	2334.98(6)	2333.96(4)
λ (Å)	1.52904	1.540598	1.540598	1.78901
instrument	SRS 8.3	X'Pert	Empyrean	Empyrean
ionic radius (Å)	0.71	0.77	0.74	0.72
crystal radius (Å)	0.57	0.63	0.60	0.58
mean X-O (Å)	1.90(1)	1.96(2)	1.89(1)	1.93(1)
mean K-O (Å)	3.349(6)	3.35(2)	3.364(6)	3.305(8)
O-Si-O variance	20.9(9.9)	183.1(130.9)	48.5(23.7)	65.9(33.1)
O-X-O variance	40.4(8.8)	230.3(125.1)	62.6(56.0)	75.3(82.6)
mean Si-O-Si (°)	140.9(10.7)	142.0(13.9)	144.7(12.6)	138.3(9.2)
mean Si-O-X (°)	130.6(9.8)	124.6(10.7)	128.1(12.5)	125.8(8.8)

Discussion

Crystal structures have been refined for $X = Fe, Zn$ and Co . These refined structures have complete T-site cation ordering and are isostructural with the $P2_1/c$ structure of $K_2MgSi_5O_{12}$. Replacing Mg with a larger X cation causes a greater distortion of the SiO_4 and XO_4 tetrahedra the silicate framework. However, the refined structures with X cations also have a smaller unit cell volume than $K_2MgSi_5O_{12}$, the mean Si-O-X angles suggest a more collapsed framework for the structures with X cations compared to $K_2MgSi_5O_{12}$. It is interesting to compare the lattice parameter errors on data collected with modern detectors to those determined from a 25 year old synchrotron X-ray powder diffraction dataset!

Conclusions

Three new crystal structures have been refined for the synthetic leucite analogues $K_2X^{2+}Si_5O_{12}$ where $X = Fe, Co$ or Zn . These refined structures have complete T-site cation ordering and are isostructural with the $P2_1/c$ structure of $K_2MgSi_5O_{12}$. However, replacing the Mg^{2+} cations in this structure with the larger Fe^{2+} , Co^{2+} , or Zn^{2+} cations causes a greater distortion of the tetrahedral units and more collapsed silicate framework structures.

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